

Stability of Bromine Intercalated Graphite Fibers

(NASA-TM-86859) STABILITY OF BROMINE
INTERCALATED GRAPHITE FIBERS (NASA) 11 p
HC A02/XF A01 CSCL 11D

N85-10187

Unclas
G3/27 24155

James R. Gaier
Lewis Research Center
Cleveland, Ohio

Prepared for the
Materials Research Society Symposium on Intercalated Graphite
sponsored by the American Physical Society
Boston, Massachusetts, November 28-30, 1984

NASA



STABILITY OF BROMINE INTERCALATED GRAPHITE FIBERS

James R. Gaier
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

SUMMARY

It has been reported that bromine intercalation compounds of crystalline graphite spontaneously deintercalate when the bromine atmosphere is removed. However, we have found that bromine intercalated P-100 graphite fibers are stable for long periods of time. They are stable under vacuum conditions, high humidity, and current densities up to 24 000 A/cm². They are thermally stable to 200° C, and at temperatures as high as 400° C still retain 80 percent of the conductivity gained by intercalation. At temperatures greater than 300° C there is significant oxidative degradation of the fibers. The environmental stability shown by the bromine compound makes it a promising candidate for practical applications in aerospace technology.

INTRODUCTION

The large mass of electrical conductor needed for electrical power distribution systems has been of concern to the aerospace industry for some time. The principal material used is copper, because of its low electrical resistivity (1.8 $\mu\Omega$ -cm) and low cost. However, copper also has a high mass density (8.9 g/cm³) and herein lies the problem. This has been the driving force for NASA's research in the use of intercalated graphite as a conductor. Graphite fibers appear particularly promising because of their convenient geometry and excellent mechanical characteristics. The density of these fibers is about 2.2 g/cm³, and they have a Young's modulus of 100 Mpsi (690 GPa) and a tensile strength of 325 kpsi (2.2 GPa) (ref. 1). While the electrical resistivity of graphite fibers is considerably higher than copper (250 $\mu\Omega$ -cm), it has been shown that intercalation can lower this resistivity to values which are competitive with copper (ref. 2).

Several other applications have been identified which utilize not only the low mass density of the fibers, but also their mechanical strength. These include signal transmission wire (where the wire size is determined by strength, not resistance), utility transmission lines and submarine cables (where strength again dominates), and space tethers. The use of these fibers to make conductive composites opens up additional applications such as lightning strike resistant aircraft skins, electromagnetic interference shielding, brushes for electric motors, and radar and communication antennae. These potential applications are detailed elsewhere (refs. 3 and 4).

In order for intercalated graphite fibers to be useful for aerospace applications, several technological problems must be solved. One of the most important is environmental stability. Intercalation is a metastable state, so the stability question is more than academic. The research reported herein addresses the problem of the environmental stability for bromine intercalated P-100 graphite fibers.

It is well known that bromine readily intercalates graphite crystals, highly oriented pyrolytic graphite (HOPG), and graphite fibers (refs. 5 and 6). For most hosts the bromine rapidly deintercalates when the graphite is removed from the bromine vapor. The result is a residue compound which contains only a small fraction of the maximum bromine intercalated. Hookey and Deitz however, report that in some carbon fibers the residue compound contains a greater fraction of bromine than the residue compounds of crystals and HOPG (ref. 6). It was further reported that relatively high temperatures were required to drive the bromine from the fibers. It was thus thought that bromine intercalated graphite fibers might have the stability required for use in applications where only modest conductivity gains are needed.

METHODS AND MATERIALS

Five environmental tests were performed on bromine intercalated graphite fibers to study their stability under the types of environmental conditions which would be encountered by the fibers in application. Fibers used in this study were Union Carbide pitch based P-100. These were chosen because they are commercially available and possess good mechanical and electrical properties (ref. 1). Although experimental fibers exist which are superior in both mechanical and electrical properties (refs. 7 and 8), these are not available to the general user, and perhaps more importantly, have not been produced in arbitrary lengths.

Before the fibers were intercalated they were heated to 350° C in air for 24 hr to remove from the surface polyvinyl alcohol which is added during their manufacture. Then the fibers were sealed in a quartz tube with a bromine reservoir, and allowed to react by vapor phase transport of bromine for about 24 hr. Experimental studies showed that increasing the reaction time to 5 days has no advantage, and that the reaction is probably complete within 4 hr. Resistivities of the intercalated fiber were typically about 50 $\mu\Omega$ -cm.

Individual fibers were mounted on sample holders which contained four-point contacts. These were either copper integrated circuit boards, or microscope slides with silver paint contacts (fig. 1). The fibers were attached to the sample holders with silver paint. Before the fibers were subjected to the environmental tests their resistance was measured. A Keithly model 225 constant current source supplied a dc current along the fiber through the outer contacts, while a Keithly model 181 nanovoltmeter measured the voltage drop between the inner contacts. The resistance of the intercalated graphite fibers was found to be ohmic, but all samples were measured at a current of 100 μ A. The fiber lengths were measured using a reticule within a Bosch and Lomb microscope to the nearest 0.1 mm. Sample fibers were approximately 1 cm in length.

The fibers were first exposed to ambient laboratory conditions for long periods of time. They were sampled first hourly, then daily, then weekly, then monthly for changes in resistance. No special precautions were taken to keep them in an isothermal environment.

A second group of bromine intercalated fibers was stored in a bell jar under a vacuum of about 10^{-7} torr (10^{-5} Pa) at ambient temperature. The fibers were removed from the bell jar to measure their resistances. Effort

was made to expose them to the ambient pressure for as short a period as possible.

A third group of fibers was subjected to a high humidity environment. This was in response to reports that ferric chloride intercalated fibers deintercalate in high humidity (refs. 9 and 10). These tests were carried out at 60° C, to generate a humidity higher than would normally be experienced by a fiber in application. The vapor pressure of water at 60° C is about 400 torr (500 Pa), approximately five times that of room temperature. The fibers were removed from the humidity chamber and allowed to cool to room temperature before the resistance measurement was made.

Thermal stability was assessed by placing different samples in muffle furnaces at 60°, 200°, 300°, 400°, 500°, and 600° C. Temperatures below 200° C showed no changes in resistivity, and those above 500° C oxidized so quickly as to make the quality of those data dubious. The temperatures were very well controlled and, outside of about 2 min to recover from the opening of the door to insert the fibers, temperature was maintained to better than 1°. To measure the resistances of the fibers, they were removed from the furnace and allowed to cool to room temperature. The reported time is that actually spent in the furnace. The resistance of the fibers was unchanged if left at ambient conditions for several hours between heating times.

The last test involved the effect of large current densities on the distribution of the intercalant. There was concern that in applications in which large dc current densities are imposed that the intercalant may migrate down the length of the fiber. The high current density test was carried out on a single bromine intercalated fiber about 15 cm in length. A 100 V potential was applied across the fiber, giving rise to an 18.8 mA current. This resulted in current density of 24 000 A/cm², which was felt to surpass that required by most applications. The fiber was subjected to these conditions for 24 days, during which the voltage fluctuation was always less than 2 percent. The fiber was then mounted on a glass slide, and contacts were painted on it with silver paint at intervals of about 5 mm along the length. Current was applied down the length of the fiber, and the voltage was measured at each 5 mm interval.

RESULTS AND DISCUSSION

The resistance per unit length (R/L) of 10 bromine intercalated P-100 fibers, at two different starting times, as a function of time since intercalation stored at ambient conditions is shown in figure 2. Analysis of the data shows the R/L for the fibers to be constant within 0.3 percent for all of the data for a time span of several months. There is a resistance increase as the fibers are removed from the bromine which is complete in about 5 min. That reaction is under study and will not be discussed here.

The R/L of six bromine intercalated fibers as a function of time stored under vacuum is shown in figure 3. It can be seen that the R/L values are insensitive to vacuum over at least month long time spans to within 1.2 percent.

Figure 4 shows the results of storing six intercalated fibers at elevated humidity for a period of weeks. Once again the R/L value is invariant (to within 0.6 percent) for each fiber.

It is noted from figures 2 to 4 that there is a large variation in R/L from fiber to fiber. How much of this variation is due to diameter variations in the fibers, to differences in the host graphite structure, or to different degrees of intercalation is presently under investigation.

The thermal stability of the bromine intercalated fibers can be assessed from figure 5. Here the average percent change in R/L for a group of six fibers at each temperature is shown, with the length of the vertical lines indicating the standard deviation of each group. There seem to be two processes occurring which define these curves. The first is a deintercalation which seems to become more complete as the temperature is raised. At 200° C there is no change, at 300° C a 15 percent increase in R/L, at 400° C a 25 percent increase in R/L, and at 500° C a 50 percent increase in R/L. However, at the higher temperatures the fibers are simultaneously oxidizing. This seems to be facilitated near the silver paint contacts. At 500° C the fibers are completely oxidized within 12 hr. The oxidation probably causes the increasing slope at long times as the temperature is increased from 200° to 500° C, and it also causes the increased deviation among the fibers at a given temperature.

The results of the high current density test are shown in figure 6. The deviation of each segment from the average R/L as a function of position along the fiber is plotted in figure 6. If the intercalant were labile, one would expect an above average deviation at one end of the fiber and a below average deviation at the other. No such trend is evident. The deviations themselves were rather large, however, and could be concealing a small trend. Some of this deviation is due to the error in determining the rather small lengths, but some may also be due to inhomogeneities within the fiber itself. This is an object for further study. The X-ray diffraction pattern of the segments at either end of the fiber showed no differences (though the patterns were admittedly weak), further indicating that, at least at these current density levels, migration under the influence of an applied electric field is not a major process.

In view of the lability of bromine in crystalline graphite and HOPG, bromine intercalated graphite fibers are surprisingly stable. Our studies show this to be true at ambient conditions for a variety of fibers including the pitch-based Union Carbide P-100, P-100-4, P-120, and an Exxon produced fiber, and the gas derived fibers produced by G. G. Tibbets at General Motors. A possible interpretation of this unexpected stability is that the fibers form a residue compound as suggested by Hooley and Deitz (ref. 6). However, the temperature stability studies appear to rule out a single residue compound, since the R/L increases to an increasing final value with the maximum temperature the fibers are exposed to. Although the micro-environment of the bromine-graphite system is postulated to be the same in fiber and crystalline forms, their deintercalation kinetics clearly differ. The greater number of defects within the fiber compared to crystalline graphite, the mechanical stresses induced when a fiber of radial geometry expands upon intercalation, and the small gross sample size, each have potential for altering the deintercalation kinetics. Clearly this is an area which begs elucidation.

SUMMARY AND CONCLUSIONS

It has been reported that bromine intercalation compounds of crystalline graphite spontaneously deintercalate when the bromine atmosphere is removed. However, we have found that bromine intercalated P-100 graphite fibers are stable for long periods of time. They are stable under vacuum conditions, high humidity, and current densities up to 24 000 A/cm². They are thermally stable to 200° C, and at temperatures as high as 400° C they still retain 80 percent of the conductivity gained by intercalation. At temperatures greater than 300° C there is significant oxidative degradation of the fibers.

The ability of bromine to improve the resistivity of graphite fibers by a factor of five or more, the ease of performing the intercalation reaction, and the environmental stability of the resulting compound as demonstrated in this paper make bromine intercalated graphite fibers an outstanding candidate for some composite materials. Electromagnetic interference shielding, lightning strike resistant aircraft control surfaces, and grounding buses are all potential applications. Yet to be determined, however, is the interaction of bromine intercalated graphite fibers with the polymer matrices with which they will be used.

REFERENCES

1. "Thornel" P-100 Carbon Fiber Grade VS-0054. Technical Information Bulletin No. 465-246, Union Carbide Corp.
2. D.W. McKee, L.V. Interrante, and R.S. Markiewicz, in Extended Abstracts and Program, 14th Biennial Conference on Carbon, American Carbon Society, pp. 276-277 (1979).
3. J.A. Woollam, H. Rashid, V. Natarajan, B. Banks, D.A. Jaworske, J.R. Gaier, C.C. Hung, and A. Yavrouian, in Extended Abstract of the Materials Research Society Symposium on Intercalated Graphite (1984).
4. J.S. Murday, D.D. Dominguez, J.A. Moran, Jr., W.D. Lee, and R. Eaton, Synth. Met. 9, 397 (1984).
5. T. Sasa, Y. Takahashi, and T. Mukaibo, Carbon 9, 407 (1971).
6. J.G. Hooley and V.R. Deitz, Carbon 16, 251 (1978).
7. G.G. Tibbetts in Extended Abstracts and Program, 16th Biennial Conference on Carbon, American Carbon Society, pp. 531-532 (1983).
8. T. Koyama, M. Endo, Y. Onuma, Jpn. J. Appl. Phys. 11, 445 (1972).
9. D.A. Jaworske in Extended Abstracts of the Material Research Society Symposium on Intercalated Graphite (1984).
10. T.S. Dziemianowicz and W.C. Forsman, Synth. Met. 8, 297 (1983).

ORIGINAL PHOTO
OF POOR QUALITY

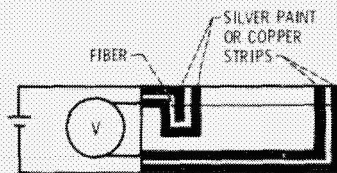
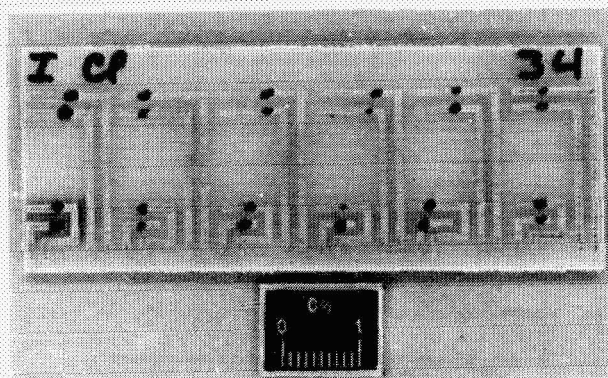


Figure 1. - Four point measurement sample holder
of the type used in the stability studies.

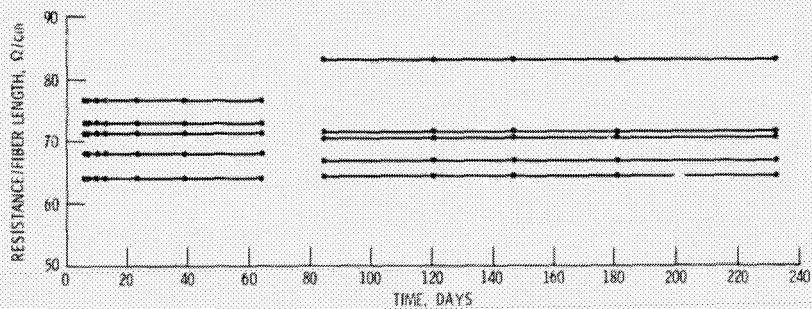


Figure 2. - Change in resistance with time of ten bromine intercalated graphite fibers at ambient conditions,

ORIGINAL FILED
OF POOR QUALITY

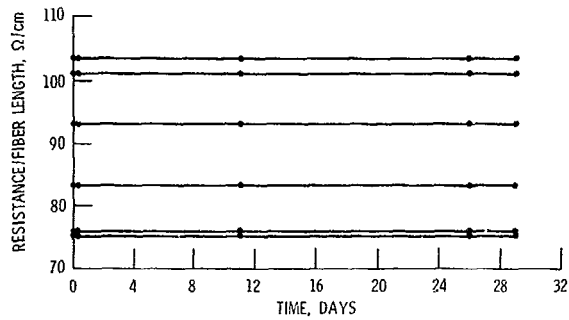


Figure 3. - Change in resistance with time of six bromine intercalated graphite fibers under vacuum.

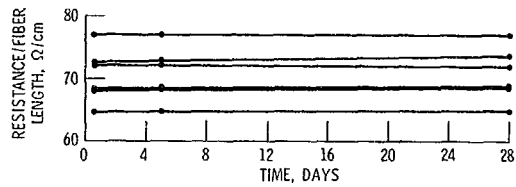


Figure 4. - Change in resistance with time of six bromine intercalated graphite fibers at 100-percent humidity at 60°C.

ORIGINAL PAGE IS
OF POOR QUALITY

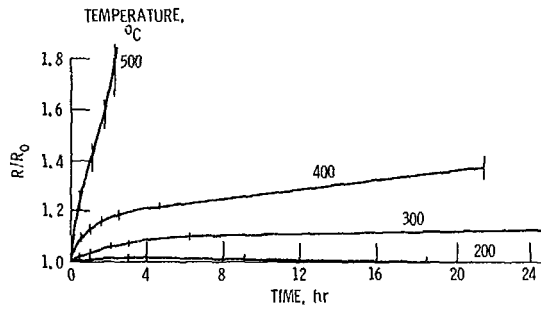


Figure 5. - Change in resistance with time of groups of bromine intercalated graphite fibers with temperature.

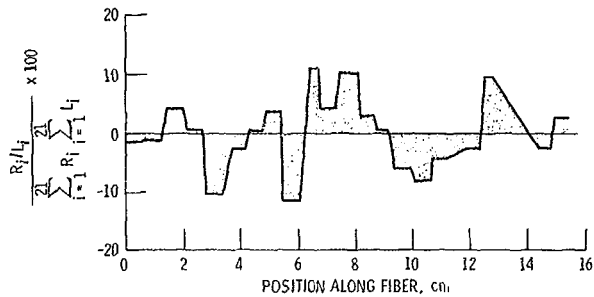


Figure 6. - Effect of high current density upon the resistance of a single bromine intercalated graphite fiber. Graph shows the deviation from the mean resistance of the resistance of twenty-one regions along the fiber length.